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Free Volume Distribution in Monodisperse and Polydisperse Poly(methyl methacrylate) Samples

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ABSTRACT: Several poly(methyl methacrylate) samples of different molecular weight and dispersity were prepared and studied by positron lifetime spectroscopy. According to the lifetime measurements, the free volume holes were smaller and their distribution was narrower in monodisperse PMMA samples than in polydisperse samples. On the other hand, density measurements revealed that the overall free volume fractions are identical in both kinds of samples. To check these results, we constructed a model for the polymer structure and calculated free volume distributions in it. Theoretical results have not shown dispersity-dependent free volume distributions which suggested that the structure of compressed PMMA pellets differs from the ideal interaction-free structure considered in calculations. This latter result emphasizes the role of entanglements in the formation of the polymer structure.

Introduction

Most polymeric materials form randomly ordered structures in the solid state. In this structure, not only the positions but also the conformations of polymer chains are determined by statistical laws. Usually, even the lengths of the chains are distributed in a wide range. Due to these features, the size of free volumes also varies from place to place in noncrystalline polymers.

Although the size distribution of free volumes is a very important parameter for the applicability of polymers (consider, e.g., corrosion protection or sealing of gas containers), its study is almost impossible using scientific methods, and developers generally use trial-and-error to produce useful polymers. Density measurements and swelling studies may provide information about the overall amount of free volumes, but in most cases, it is not enough to characterize the free volume properties of a polymer. Due to the complexity of the problem, even theoretical calculations had limited power in this field earlier, but recent calculations gave encouraging results,[1,2] determining sizes and shapes of free volume holes in a model material.

For studying the size distributions of free volume holes experimentally, positron lifetime spectroscopy proved to be a valuable tool. The lifetime of positrons and orthopositronium (o-Ps) atoms are known to be determined by the size of the free volume holes.[3] Different methods were developed to evaluate lifetime distributions from positron lifetime spectra,[4,5] and recently, most authors conclude that free volume distributions of polymers can be calculated from these lifetime distributions.[6] Even skeptics yield that lifetime distributions represent free volume distributions, although the method should be calibrated for materials of different chemical and physical structure.

In this work, we studied PMMA samples of different molecular weight and dispersity by positron lifetime spectroscopy. As the chemical composition and the preparation method were the same for every sample, we supposed that all possible differences should be related to the different size distribution of free volume holes. We evaluated o-Ps lifetime distributions from spectra and studied them to decide whether polydispersity has any effect on the size distribution of free volumes.

To simplify the interpretation of positron lifetime data, we constructed a model to calculate theoretical free volume distributions. The model is a simplified representation of the polymer structure, but this simplification was necessary to gain reasonable computation times.

Simulated Polymer Structures

In our model, the continuous space was replaced with a lattice of separated points. The points were ordered so that they copied the perfect diamond lattice in which every vertex (lattice position) has tetrahedral symmetry. Carbon atoms were allowed to be situated at empty vertexes but not between them. Polymeric chains were ordered so that they followed paths determined by covalent bonds of the supposed diamond lattice. This provided chains in which the CCC angles were exactly 109.5°. We studied lattices constructed of 5×10^6, 3.2×10^7, and 1.25×10^8 vertexes, respectively, but all calculations provided similar results.

The first step of the calculation was the filling of the lattice with random chains. A starting point was chosen randomly in the lattice, and a chain was built up following the supposed covalent bonds of the lattice. At every vertex a direction was chosen at random from the available three (Figure 1). Choosing vertexes already filled was restricted and the decision procedure repeated if it provided such a lattice position. When the desired length of the chain was reached, a new starting point was chosen randomly and a new chain was built up. This procedure continued until a certain number of chains were built up, and finally, we obtained a lattice in which “lattice positions” were filled randomly. Filled vertexes marked the atoms of polymer chains, and empty spaces represented free volumes. It is very important to note here that during the construction of chains no interaction other than mutual exclusion was

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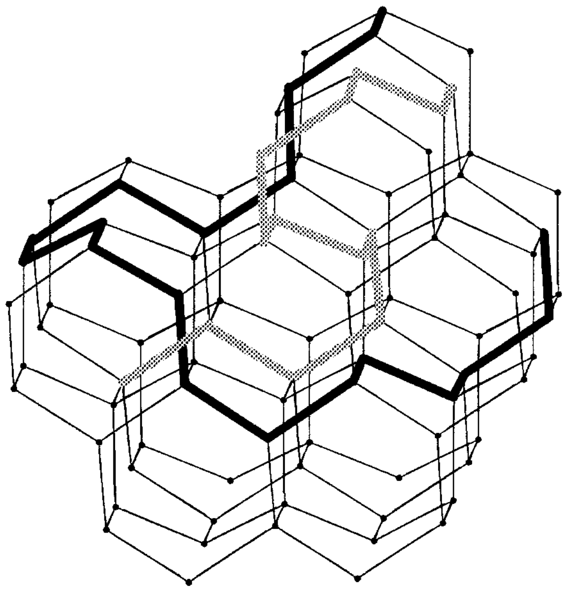

Figure 1. A section of the diamond lattice used in the calculations. Points at the vertexes indicate empty crystal positions, and the differently colored thick lines indicate sequences of two separate polymer chains. At the end of the calculations, almost four-fifths of crystal positions were filled with the chains.

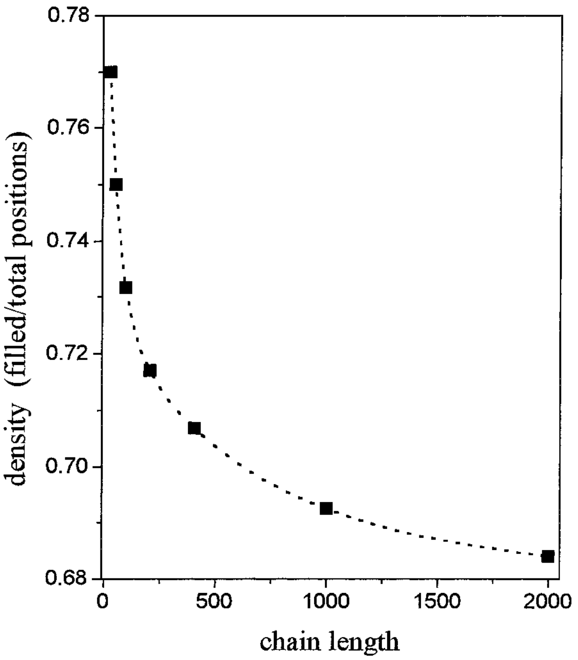

Figure 2. Densities calculated for the simulated polymers vs chain length. Here density is defined as the proportion of filled crystal positions to all the possible positions of the lattice. Note that in this system the CCC angles are exactly 109.5°, and no interaction is supposed between the chains other than mutual interaction.

allowed, and so the obtained structure represents an ideally interaction-free polymer.

The number of chains was determined so that we gain comparable data even if the length of chains varies. This was reached by fixing the ratio of the number of lattice positions and the number of atoms in all the chains. To take the well-known effects of chain length into account, we allowed the chains to leave the lattice. When a chain left the considered lattice, its calculation was stopped and a new chain was started from another point. This procedure provided a "density" for the calculated "polymers" which decreased with increasing chain length, but the "density" seemed to saturate rapidly (Figure 2). Note that the observed small density decrease might well be artificially introduced by the calculation method without any physical consequence.

After the "polymer structure" was built up, free volumes were investigated. To avoid problems raised by differently shaped holes, we did not try to gain free volume size distributions. Instead, we calculated local density at different points and compared the distributions of this parameter. One million random lattice positions were chosen in every case. The local density was represented by the number of empty vertexes in the first three "coordination spheres" of the chosen vertex. Several calculated distributions of this parameter are shown in Figure 3. Figure 3a presents the effects of chain length in a more detailed way than "density" values in Figure 2. Figure 3b shows the effects of the assumed "density" (i.e., the ratio of filled positions/lattice positions) on local density distributions.

The distributions given in Figure 3 were calculated for monodisperse chains; however, choosing polydisperse chains did not modify the results. Gaussian and gamma distributions of different widths were tried for the description of chain length distributions, but the distribution of local density did not change until the average chain length was the same. This result suggests that we cannot expect differences in free volume size distributions in monodisperse and polydisperse polymers which are similar to our model. Let us emphasize some characteristic features here for such polymers: binding angles are near 109.5°; chain length does not effect the shape of chains; the chains are totally independent (no cross-links, no secondary binding forces); and the chains are linear (no long side chains).

Polyethylene, which was studied by positron lifetime spectroscopy several times, might be a good candidate for such a polymer. Positron lifetime measurements[7-10] seem to confirm these assumptions, as the authors have never mentioned dispersity-dependent lifetime data. Moreover, all the different experiments, performed by different authors over a long time, provided very similar lifetime data for amorphous polyethylene, independently of molecular weight or polydispersity.

Another example for the use of the model is provided by PEEKK samples (poly-ether-ether-ketone-ketone), where the mean lifetime of o-Ps atoms is not affected by polydispersity at all (Figure 4). In this latter case o-Ps lifetime was found to be dependent on molecular weight and the conditions of sample preparation[11] (pressure) but proved to be independent of polydispersity over a very wide range (from 2 to 8). The data indicate that, in the case of PEEKK, our model is applicable, and the size of free volume holes depends on molecular weight but is not altered by polydispersity of the polymer.

Our present sample material PMMA might differ a little from the ideal polymer of the model because it has short, slightly polar side chains.

Experimental Part

Narrowly distributed PMMA standards were obtained from Aldrich, and the broadly distributed PMMA samples were prepared by radical polymerization.

Polymerization of methyl methacrylate (MMA) (Aldrich) was carried out in 25 mL Schlenk tubes, equipped with a rubber septum and magnetic stirrer bar. 2,2′-Azobis(isobutyronitrile)

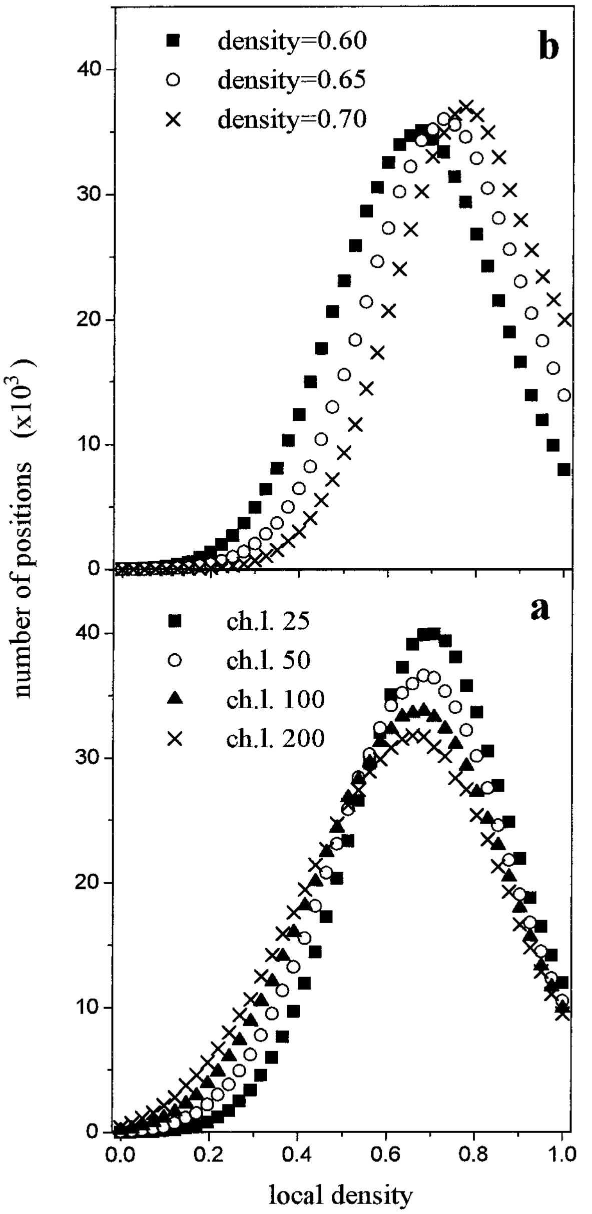

Figure 3. Local density distributions in the simulated polymer calculated for several different chain lengths (a) and densities (b). Calculations were performed for a lattice containing 500 × 500 × 500 positions, and local densities were determined at 1×10^6 random points after the simulated polymer structure was built up. Local density was defined as filled positions per possible positions in the nearest neighborhood of every vertex up to the third shell. For chain length dependence calculations (a) the density was set to 0.65, and for the density dependence calculations (b) the chain length was set to 200.

(AIBN) (Aldrich) was applied as radical initiator and recrystallized from diethyl ether prior to use. MMA was purified by vacuum distillation from CaH_2. Initiator and monomer were added into the Schlenk tube and degassed by three consecutive freeze–thaw cycles prior to polymerization. Initiator concentrations, reaction times, and reaction temperatures are listed in Table 1. The polymer was isolated by precipitation in methanol, washed, and dried under vacuum at 60 °C.

Molecular weights were determined by means of size exclusion chromatography (SEC), calibrated with PMMA standards, using THF as solvent. However, the exact molecular weight distributions were provided by this method; the dispersity values given in Table 1 and used to produce the figures are represented below by the polydispersity index: $D = M_w/M_n$. For our purposes (i.e., to show the dispersity dependence of free volume distributions) this representation is adequate.

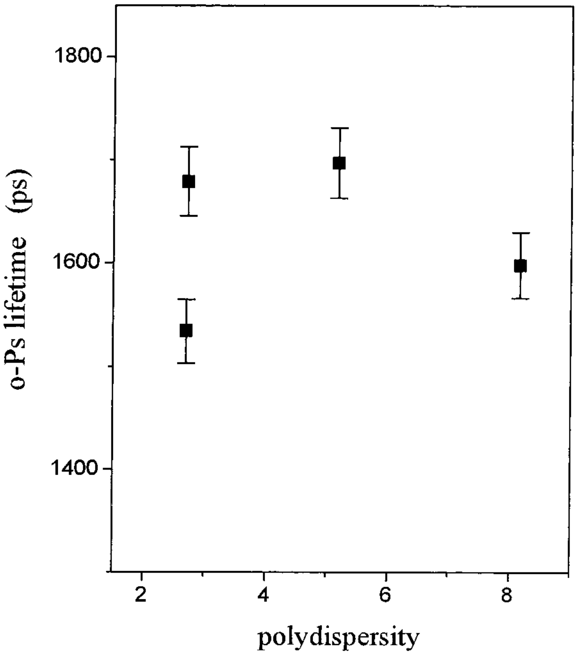

Figure 4. Mean o-Ps lifetimes observed in several PEEKK samples. In these samples, in accordance with the predictions of the model, o-Ps lifetimes were found to be dependent on molecular weight[11] but not on polydispersity.

Table 1. Reaction Conditions, Molecular Weights, and Dispersities for the Synthesis of Broadly Distributed PMMA Samples[a]

polymer	[AIBN] (10^{-2} mol/L)	temp (°C)	reaction time (h)	M_n ($\times 10^3$)	M_w ($\times 10^3$)	D
74	4.45	90	1.5	38	74.3	1.95
84	4.92	60	24	45.5	118	2.59
76	4.42	60	72	66.9	172.5	2.57
90	4.73	60	6	12.3	16.5	1.34
100	2.31	60	6	138.1	443.2	3.20
89	0.95	60	6	257.2	772.6	3.00

[a] The four monodisperse samples were PMMA standards obtained from Aldrich, and the mixed "artificial" sample was prepared from these standards.

For positron lifetime measurements, the polymer powders were compressed into tablets by hydraulic press with 10 kN pressure. The compression temperature was kept at 120 °C, i.e., above T_g, which allowed a large molecular mobility during the preparation process. The samples were transparent tablets, and their density was around 1.15 g/cm^3, independent of molecular weight and dispersity.

Positron lifetime spectra were measured using a standard lifetime spectrometer, based on a fast–fast coincidence system. The time resolution of the spectrometer was around 210 ps. Every spectrum contained 5×10^6 counts, allowing reliable evaluations. The spectra were recorded at 20 °C, i.e., below T_g.

The lifetime spectra were evaluated by two methods. The conventional method[12] supposes that lifetime spectra of polymers are composed of three or four exponential curves, each representing different positron states. In PMMA three lifetime components were observed, among which the longest one is the most useful for the characterization of polymers. This component is the mean lifetime of orthopositronium (o-Ps) atoms. For these evaluations the RESOLUTION computer program[12] was used.

The second evaluation method supposes that each o-Ps is localized in a free volume hole before its annihilation. Thus, their separate lifetimes produce a distribution that can be related to the size distribution of free volumes. For these evaluations a variation of the MELT computer code[5] was used.

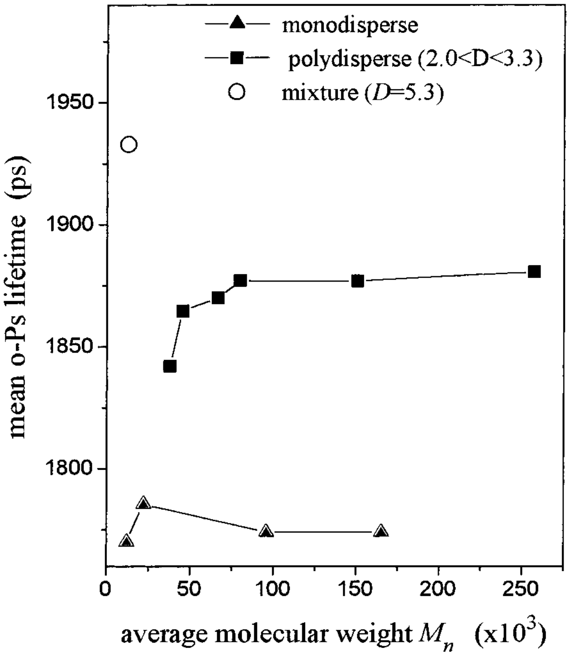

Figure 5. Mean o-Ps lifetimes vs molecular weight M_n in various PMMA samples. The o-Ps formation intensity, i.e., the percentage of positrons forming o-Ps, was around 23% in every case. The open circle and the “mixture” label indicate the “artificial” polydisperse sample prepared by mixing several monodisperse samples.

Results and Discussion

Figure 5 shows the mean o-Ps lifetimes gained by the standard evaluation method. The most interesting result is the significant difference between the monodisperse and polydisperse samples. The lifetime measured in monodisperse samples is shorter and independent of the molecular weight (chain length). On the other hand, beyond the significantly longer values, o-Ps lifetime shows molecular weight dependence in polydisperse samples. Using the most widely used approximation,[13] the size of free volumes can be calculated from the o-Ps mean lifetime values by simple equation

$$\tau = \frac{1}{2}\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1} \qquad (1)$$

where R is the radius of the spherical voids, $R - R_0$ is the penetration depth of o-Ps into the bulk, and τ is the lifetime of o-Ps. This method provides R = 2.65 Å for monodisperse and R = 2.70−2.75 Å for polydisperse samples, which represents a very small but significant difference.

These results indicate that the structure of PMMA differs from the ideal structure considered in the calculations, and dispersity does have an effect on the size distribution of free volumes in this case. This result is emphasized by Figure 6 where the lifetime values are given vs dispersity. This curve is definitely smoother than any of the lifetime vs molecular weight curves.

The assumption of lifetime distribution instead of a mean lifetime provided very similar results (Figure 7). The mean of the lifetime distributions obtained for monodisperse samples was always observed at shorter lifetimes than for polydisperse samples. Note that the short lifetime “starting points” of the distributions were almost identical (Figure 7), but polydisperse samples provided broader distributions. Considering eq 1, this means that the sizes of the smallest free volumes are identical in monodisperse and polydisperse samples, but polydisperse samples contain large voids as well, which are not present in monodisperse samples. Note that the integrals of the lifetime distributions given in Figure 7 are almost identical, indicating that the integrated free volumes of the different samples are the same. This fact agrees with the measured density values which did show neither molecular weight nor dispersity dependence.

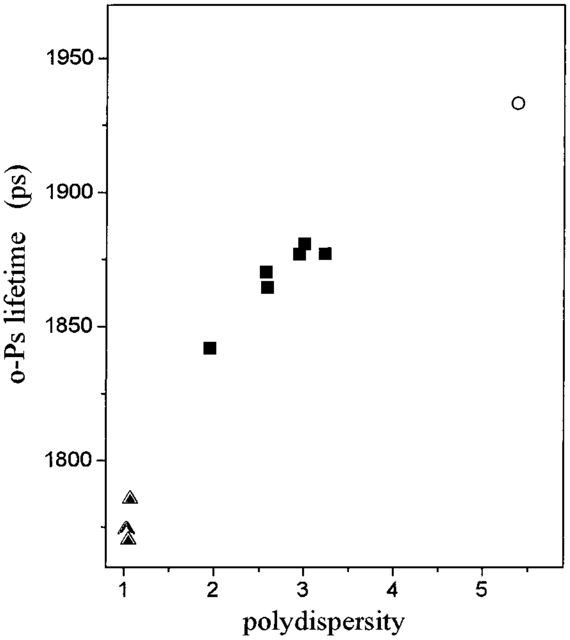

Figure 6. Lifetime values of Figure 5 vs polydispersity.

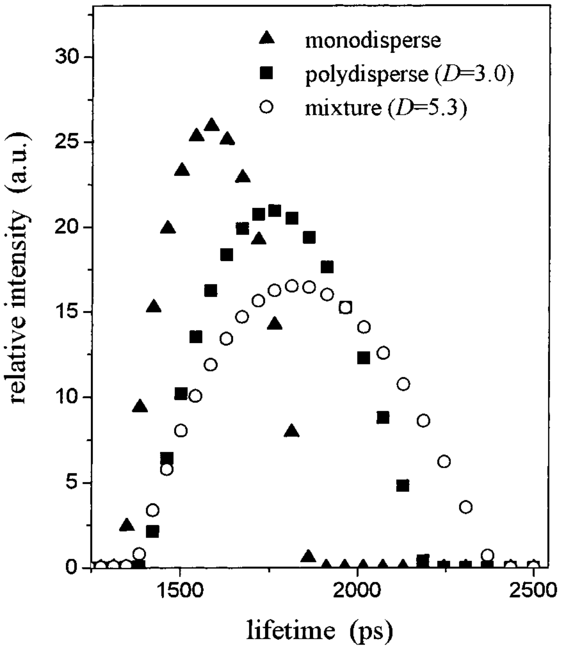

Figure 7. Lifetime distributions obtained for three PMMA samples by the analysis of lifetime spectra. These lifetime distributions are related to free volume size distributions by eq 1. The widths of the observed distributions are dependent on dispersity, but the coincident starting points at the left-hand sides of distributions indicate that the size of smallest voids is the same in every sample.

To confirm the dispersity dependence of lifetime data and exclude false effects, produced possibly by the different synthetic methods, an “artificial” polydisperse sample was prepared. This highly polydisperse sample was prepared by mixing several monodisperse polymers. As the open circles show in Figures 5−7, both the lifetime value and the lifetime distribution of this “artificial” sample emphasize the dispersity dependence of free volume size. Consequently, PMMA does not fulfill the expectations of the model, and we should find a reason explaining dispersity-dependent free volume size.

The differences between model calculations and experiments might be explained by the sample preparation conditions. The large pressure applied for tablet preparation should have decreased the original sizes of the free volume holes. According to lifetime results, this decrease is dependent upon the molecular weight dispersity.

One explanation for this is provided by entanglements, which were ignored in the calculations. Above a certain critical molecular weight ($M_{cr} = 30\,000$ for poly(methyl methacrylate)[14]), the polymer chains are considered entangled. These entanglements help to keep the polymer chains in position, making them elastic and resistant to irreversible deformations. This is evident in viscometry measurements, whereby at $M_n > M_{cr}$ viscosity increases rapidly with M_n. At molecular weights below M_{cr}, the viscosity increase is not as dramatic, and entanglement forces are considered negligible.[14]

In monodisperse samples with $M_n > M_{cr}$, each polymer chain is localized by approximately the same force, and the applied pressure and temperature increase therefore has a similar effect on the individual chains. Consequently, the free volume changes should also be relatively uniform.

In polydisperse samples, however, shorter, more mobile molecules are also present which might change the free volume distribution on deformation. On application of pressure and temperature increase, the shorter, more mobile chains should be capable of moving to fill in some holes. The remaining holes and the new holes that are created by the movement of the smaller chains cannot be filled because of the immobility of the larger polymer chains. This leaves a sample with a higher dispersity of free volume spaces.

Conclusions

A model was constructed to study size distribution of free volume holes in polymers. The model describes most of the well-known features of linear chain apolar polymers very well. It proved that the model approximates the molecular weight dependency of density and free volume distribution in the expected way: no difference was observed between monodisperse and polydisperse polymers.

On the other hand, the positronium lifetime study revealed that PMMA samples diverge from the predictions of the model and the free volume distribution does depend on dispersity. The cause of this divergence might be the combined effects of sample preparation (high pressure and temperature) and entanglements of polymer chains.

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References and Notes

(1) Rigby, D.; Roe, R. J. *Macromolecules* **1990**, *23*, 5312.

(2) Vleeshouwers, S.; Kluin, J.-E.; McGervey, J. D.; Jamieson, A. M.; Simha, R. *J. Polym. Sci., Part B: Polym. Phys.* **1992**, *30*, 1429.

(3) Brandt, W.; Berko, S.; Walker, W. W. *Phys. Rev.* **1960**, *120*, 1289.

(4) Gregory, R. B.; Zhu, Y. *Nucl. Instrum. Methods Phys. Res. A* **1990**, *290*, 172.

(5) Shukla, A.; Peter, M.; Hoffmann, L. *Nucl. Instrum. Methods A* **1993**, *335*, 310.

(6) Schrader, D. M.; Miller, B. N. *Mater. Sci. Forum* **1995**, *175*, 1021.

(7) Bertolaccini, M.; Bisi, A.; Gambrini, G.; Zappa, L. *Appl. Phys.* **1978**, *17*, 203.

(8) Serna, J.; Abbé, J. Ch.; Duplatre, G. *Phys. Status Solidi A* **1986**, *98*, 171.

(9) Serna, J.; Abbé, J. Ch.; Duplatre, G. *Phys. Status Solidi A* **1989**, *115*, 389.

(10) Consolati, G.; Quasso, F. *Appl. Phys.* **1990**, *50*, 43.

(11) Süvegh, K.; Klapper, M.; Vértes, A. *J. Radioanal. Nucl. Chem. Lett.* **1994**, *186*, 375.

(12) Kirkegaard, P.; Eldrup, M.; Mogensen, O. E.; Pedersen, N. J. *Comput. Phys. Commun.* **1981**, *23*, 307.

(13) Liu, J.; Deng, Q.; Jean, Y. C. *Macromolecules* **1993**, *26*, 7149.

(14) van Krevellen, D. W. In *Properties of Polymers, Their Estimation and Correlation with Chemical Structure*; Elsevier: Amsterdam, 1976; pp 331−393.

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